

# Phase Stability Calculations in the Pu-N and Pu-O Systems

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## Summary

The assessment of the Pu-PuN pseudo-binary phase diagram was performed using an optimization algorithm to calculate the interaction parameters in the excess Gibbs free energy of binary solutions. The procedure allows for retrieving the Gibbs free energy of all phases, to be used in calculations of phase equilibrium of multi-component systems. The free energy of  $\text{PuO}_{2-8}$  was modeled and used to calculate the pressure of oxygen as a function of temperature and composition with impact on the calculated Pu-O phase diagram.

## 1. Introduction

In order to model the thermodynamic properties of nitrides and oxides we have collected data from literature and from the available commercial databases like Barin, JANAF, CODATA, Pankratz [1-4]. The modeling process consisted in analyzing the data using an uncertainty evaluation procedure based on Bayesian statistics. A polynomial function in temperature was used as a model for the heat capacity:

The Gibbs free energy of each component of the Pu-PuN system, for each phase, was fitted to:

$$G_{\text{component}}^{\text{phase}}(T) = a + bT + cT \ln T + dT^2 \quad (1)$$

Where T is the temperature in K degrees.

The minimum number of fitting terms was decided after a careful analysis of the standard deviation and the correlation factor. The analysis proved that additional terms would not significantly increase the precision of the fitting.

We have developed a set of computer programs that is capable of checking the self-consistency of the data set by verifying the fundamental thermodynamics relationships, which involve the heat capacity at constant pressure  $C_p$ , the entropy S, the enthalpy H and the Gibbs free energy G. If the pressure is constant, then:

$$H(T > T_1) = H_{T_0} + \int_{T_0}^{T_1} C_{p1}(\tau) d\tau + \Delta H_{T_1} + \int_{T_1}^T C_{p2}(\tau) d\tau \quad (2)$$

$$S(T > T_1) = S_{T_0} + \int_{T_0}^{T_1} \frac{C_{p1}(\tau)}{\tau} d\tau + \frac{\Delta H_{T_1}}{T_1} + \int_{T_1}^T \frac{C_{p2}(\tau)}{\tau} d\tau \quad (3)$$

$$G(T) = H(T) - T \cdot S(T) \quad (4)$$

where  $T_1$  is the temperature of the phase transformation (if any) and  $T_0$  is the reference temperature for enthalpy and entropy. Additional terms have been included to describe subsequent phase transformations. In many commercial databases,  $T_0$  equals 298.15 K because only high temperature properties are of interest. Our program also models properties situated below room temperature.

A more difficult problem is the modeling of the Gibbs free energy of solutions and non-stoichiometric compounds. That involves not only the knowledge of the thermodynamic properties of the components but calculations regarding the interaction parameters.

The Gibbs free energy of the phases in a binary system was modeled using:

$$G^{phase}(T, x_1, x_2) = x_1 G_1^{phase}(T) + x_2 G_2^{phase}(T) + G^{mix, phase}(T, x_1, x_2) \quad (5)$$

where  $x_1$  and  $x_2$  are the mole fractions and the mixing Gibbs free energy of each binary phase is given by:

$$G^{mix, phase}(T, x_1, x_2) = RT(x_1 \ln x_1 + x_2 \ln x_2) + G^{ex, phase}(T, x_1, x_2) \quad (6)$$

Here the excess Gibbs free energy is a function of interaction parameters,  $\Omega$ .

$$G^{ex, phase}(T, x_1, x_2) = x_1 x_2 \Omega_1(T) + x_1 x_2 (x_1 - x_2) \Omega_2(T) + x_1 x_2 (x_1 - x_2)^2 \Omega_3(T) \quad (7)$$

The interaction parameters are temperature dependent:

$$\Omega_i(T) = A_i + B_i T + C_i T \ln T \quad (8)$$

where  $i = 1, 2$ , or  $3$ .

It is useful to note that the composition variables are not independent and they must add up to unity:

$$x_1 + x_2 = 1 \quad (9)$$

Using the change of variables:

$$\begin{aligned} x_1 &= 1 - x \\ x_2 &= x \end{aligned} \quad (10)$$

One could retrieve the classical forms:

$$G^{phase}(T, x) = (1 - x) G_1^{phase}(T) + x G_2^{phase}(T) + G^{mix, phase}(T, x) \quad (11)$$

$$G^{phase}(T, x) = RT((1 - x) \ln(1 - x) + x \ln x) + G^{ex, phase}(T, x) \quad (12)$$

$$G^{ex, phase}(T, x) = (1 - x)x \Omega_1(T) + (1 - x)x(2x - 1) \Omega_2(T) + (1 - x)x(2x - 1)^2 \Omega_3(T) \quad (13)$$

## 2. The Pu-N System

The uncertainty regarding the phase equilibrium in the Pu-N phase diagram is perhaps best emphasized by the dotted lines in the phase diagram published in the Masalski collection of phase diagrams [5]. Although qualitatively, the diagram in Fig. 1 is accepted as the best available description of the system, the solubility limit and the liquidus line are still uncertain. There is a general agreement that actinide mononitrides have narrow homogeneity ranges toward the hypostoichiometric side [6, 7]. To describe the non-stoichiometry of the  $AN_{1-x}$  compounds, where A is an Actinide element, the sublattice formalism was often used [8-10]. Rarely the phase boundaries are determined [11] and that is only for specific temperatures. The heat capacity of plutonium nitride was experimentally determined [12,13] or modeled using molecular dynamics method [14]. More information is available for the partial pressure of vapor species. [15-21].

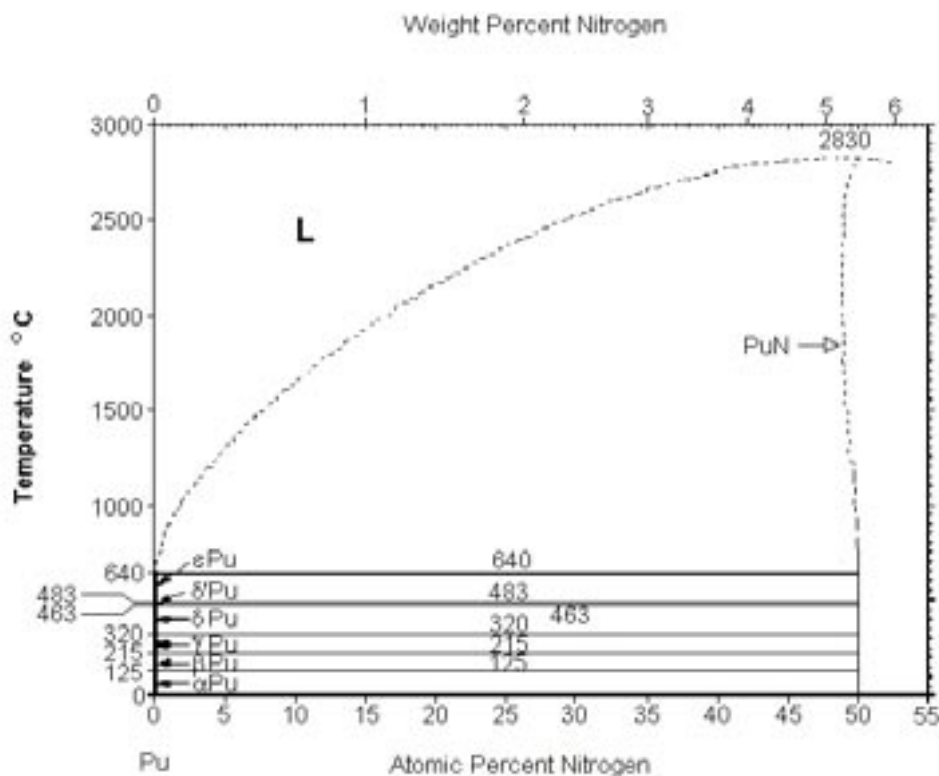


Figure 1. The Pu-N phase diagram reported by Massalski [5].

## 2.1 Thermodynamic Properties of the Components

The thermodynamic properties of Pu and PuN have been studied and the free energy fitted to functional forms described in Eq. 1. The results are presented in Table 1.

Table 1. Coefficients for the Gibbs Free Energy of Pu and PuN Phases

	$I$	$T$	$T \ln T$	$T^2$
	a	b	c	d
Pu alpha	-9864.403604	169.427558	-32.949671	-0.000241
Pu beta	-1048.25773	2.331061	-6.631356	-0.032083
Pu gamma	-400.645568	15.147574	-9.397931	-0.026012
Pu delta	-9208.601699	226.449155	-42.957889	0.004057
Pu delta prime	-379566.347	6763.945761	-1030.425454	0.661948
Pu eta	2723.805359	63.014846	-19.071663	-0.010073
Pu liquid	-6936.951655	219.630205	-41.843728	0.000001
PuN solid	-294493.186	-42.724	19.589	-0.009
PuN liquid	-309117.786	143.062	-6.32	0

## 2.2 Assessment of the Pu-PuN Phase Diagram

Due to the large uncertainty in the Pu-N phase diagram, we decided to use the pseudo-binary system Pu-PuN. One could prove that the models for the two systems are equivalent. The main problem was the calculation of the interaction parameters in the excess Gibbs free energy, that is, to retrieve the values of the A, B, and C coefficients in Eq. 8. A set of data points extracted from the Masalski phase diagram along the phase equilibrium lines was used as a target for the optimization procedure (see Table 2). The selection took into account the curvature of the lines and the minimum number of elements of the data set required to ensure that the optimization problem is correctly defined.

**Table 2. Data Points from Massalski's Diagram**

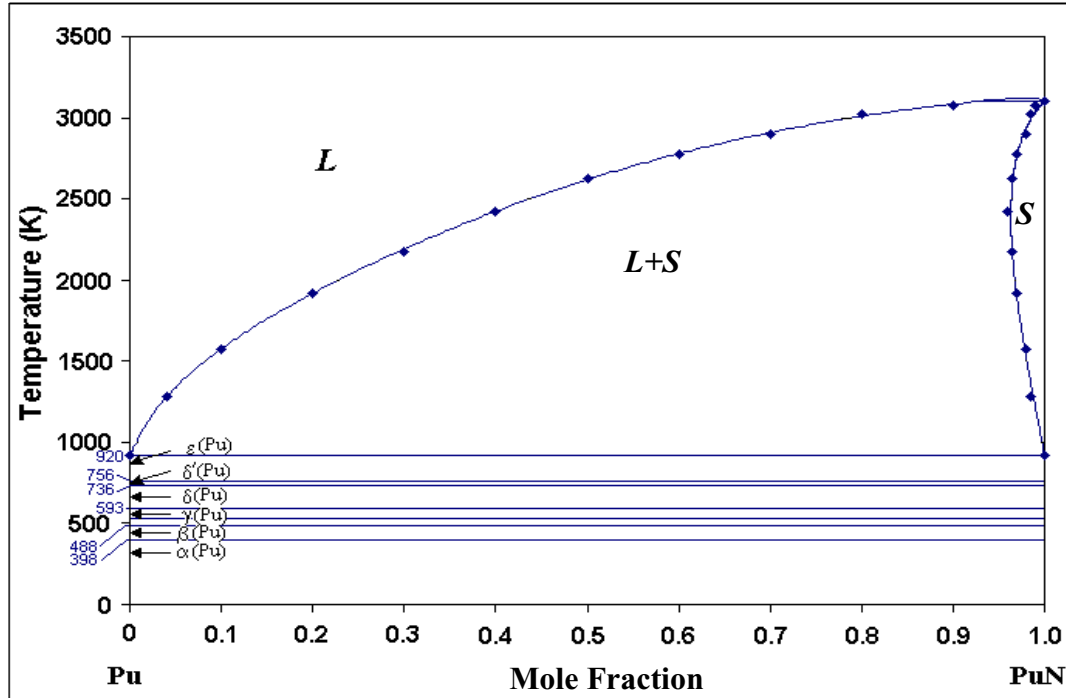
Temperature (K)	$x^L$	$x^S$
920	0	1
1275	0.04	0.984
1575	0.1	0.98
1925	0.2	0.97
2175	0.3	0.964
2425	0.4	0.96
2625	0.5	0.964
2775	0.6	0.97
2900	0.7	0.98
3025	0.8	0.984
3075	0.9	0.99
3103	1	1

The CALPHAD type optimization procedure [22] was performed using the WinPhad software [23] and was quite cumbersome since the program required reasonable initial guesses for all parameters. Table 3 shows the results of the optimization procedure for all phases in the binary system Pu-PuN.

**Table 3. Coefficients of the excess Gibbs free energy interaction parameters in the Pu-PuN pseudo-binary system**

	<b>1</b>	<b>T</b>	<b>T ln T</b>
<b>Liquid</b>	<b>A</b>	<b>B</b>	<b>C</b>
$x_1x_2$	34020912.100976	-61986.22406	6008.786992
$x_1x_2(x_1-x_2)$	-37355531.622450	64314.63751	-6569.724775
$x_1x_2(x_1-x_2)^2$	3981647.075148	10600.79375	-1435.561709
<b>Solid Solution</b>			
$x_1x_2$	83292913.154202	-34693.19096	2307.956408
$x_1x_2(x_1-x_2)$	117205328.211160	19046.37316	-4409.421512
$x_1x_2(x_1-x_2)^2$	37586343.852412	44531.8003	-5947.475464

A comparison of the calculated phase diagram and the data set used as a target for the optimization is presented in Fig. 2. The agreement is very good and the correlation factor was 0.93 for the liquidus line and 0.91 for the solid solution line.



**Figure 2. Comparison of the calculated phase diagram and data points from the Masalski phase diagram.**

### 3. Thermodynamic calculations in the Pu-O system.

There is no complete assessment of the Pu-O phase diagram. An effort of unifying various versions of the diagram was started at LANL [24] but never completed. Different regions of the diagram have been explored by experimental means [25-35] and rarely thermodynamic calculations have been carried out [36-39]. Fig. 3 emphasizes the complexity of the phase equilibrium in this system and the necessity of accurately determining of the equilibrium lines, mainly at high temperatures.

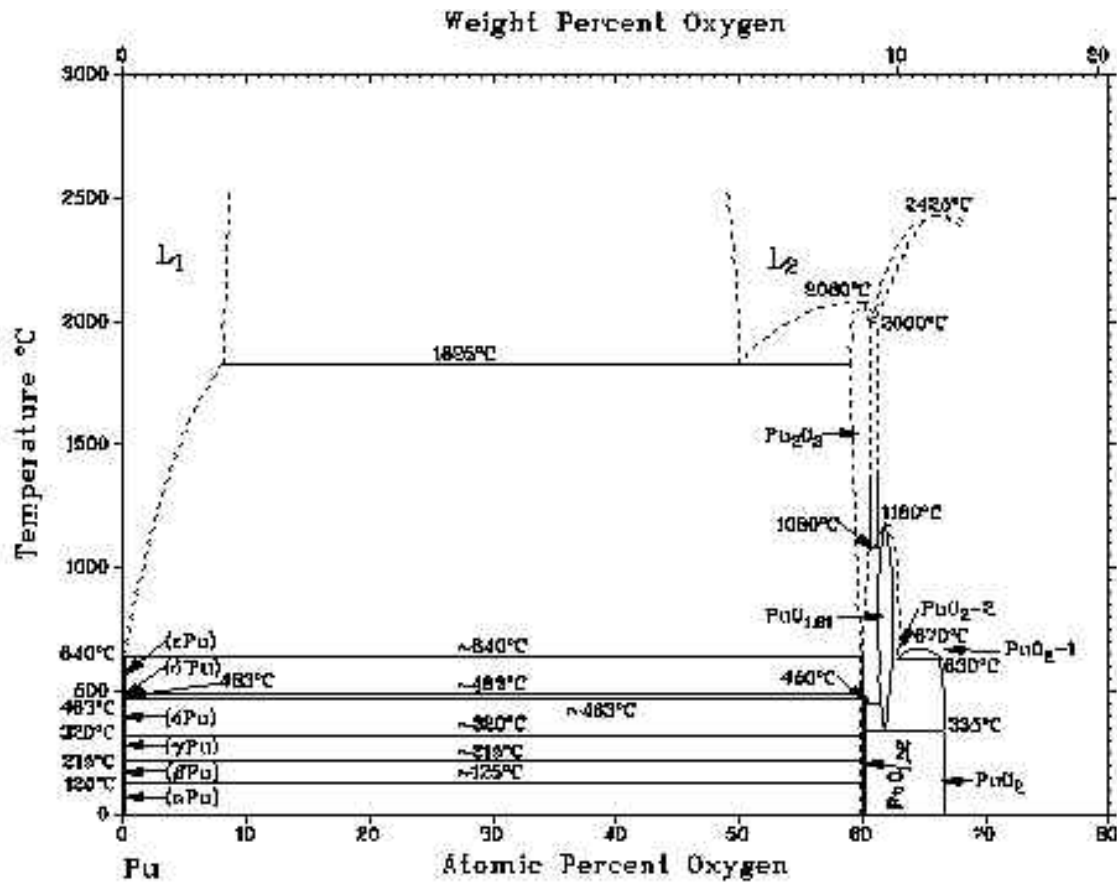


Figure 3. The Pu-O phase diagram reported in the Massalski book [5].

### 3.2 A model for the Gibbs free energy of non-stoichiometric plutonium oxide.

As a step towards the complete assessment of the Pu-O phase diagram we modeled the thermodynamic properties of the sub-stoichiometric ceria.  $\text{PuO}_{2-\delta}$  was modeled as a solution of  $\text{PuO}_2$  and  $\text{Pu}_2\text{O}_3$ , using a regular interaction parameter proposed by Besmann *et al.* [38,39]:

$$\Omega_1(T) = -63470 + 49.36T \quad (\text{J/mol}) \quad (14)$$

The model allows for the calculation of the Gibbs free energy of  $\text{PuO}_{2-\delta}$  as a function of temperature for various sub-stoichiometry cases situated between  $\delta = 0$  ( $\text{PuO}_2$ ) and  $\delta = 0.5$  ( $\text{Pu}_2\text{O}_3$ ). In Fig. 4 it is important to note the change in the curvature of the Gibbs free energy function between room temperature and 3000 K. That will account for the liquidus line in the phase diagram, where liquid immiscibility might occur. That is even more apparent in the plot of the mixing Gibbs free energy of formation (as defined in Eqs. 6 and 12). Figure 5 emphasizes the large and positive Gibbs energy of mixing at high temperatures.

A more sophisticated atomistic model that accounts for the mobility of oxygen atoms is under development.

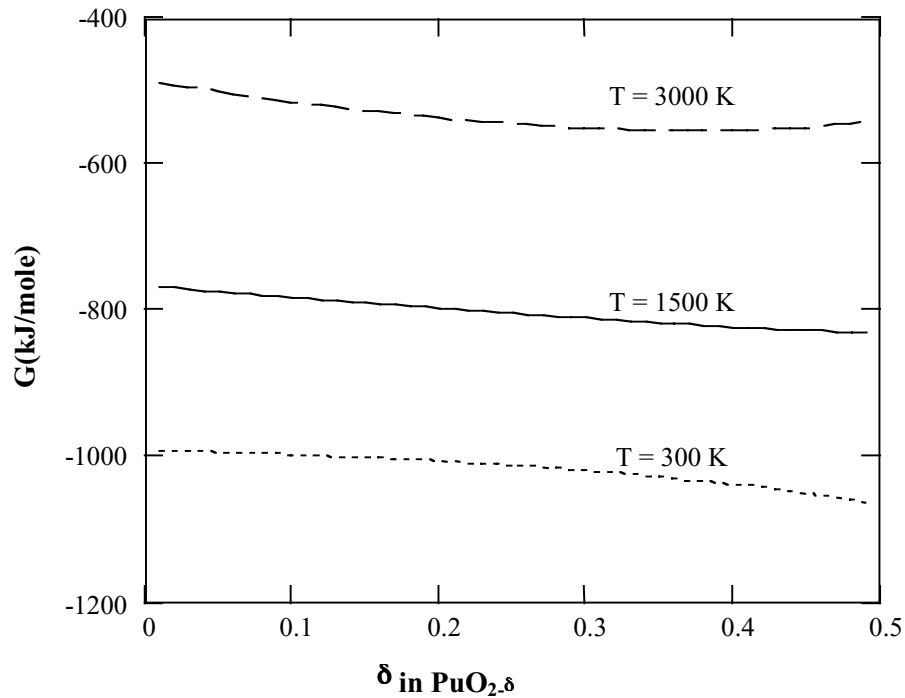


Figure 4. Gibbs free energy of  $\text{PuO}_{2-\delta}$ .

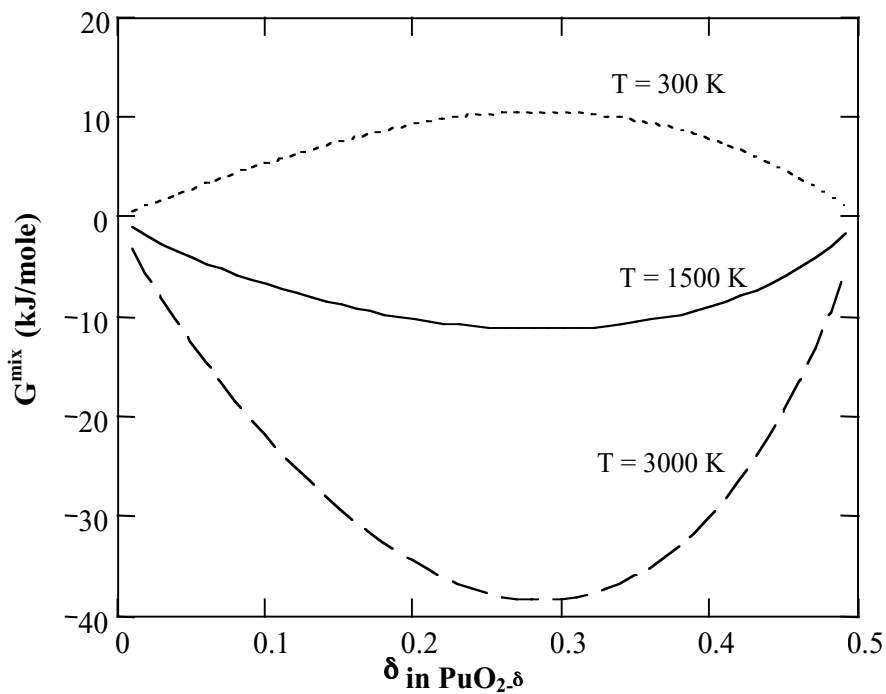
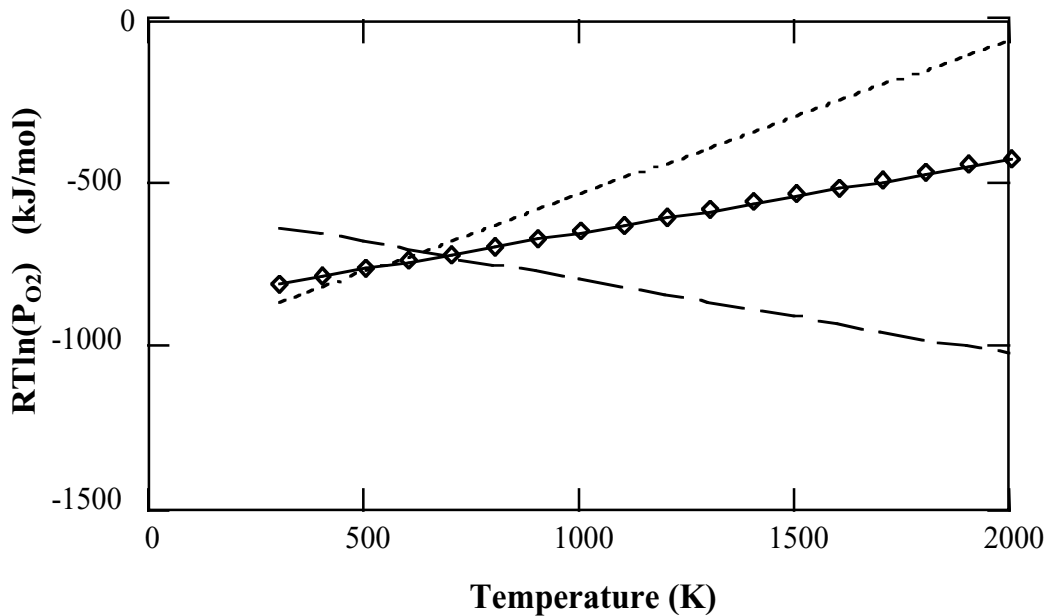


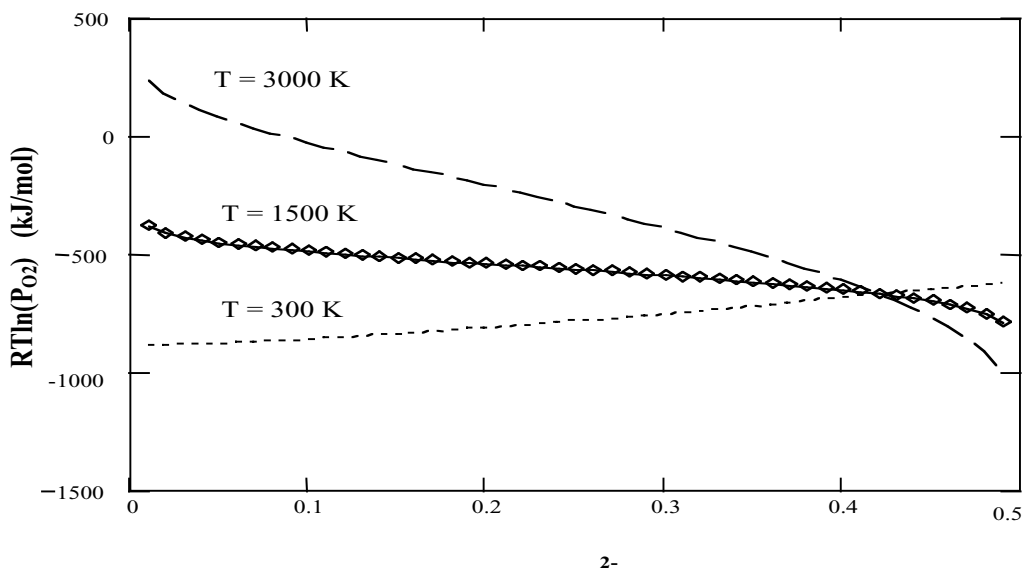
Figure 5. Mixing Gibbs free energy of  $\text{PuO}_{2-\delta}$ .

### 3.2 Calculation of the partial pressure of oxygen in non-stoichiometric plutonium oxide.

The Gibbs free energy model was used for the calculation of the partial pressure of oxygen in non-stoichiometric plutonium oxide, as a function of temperature and composition. The results are presented in Figs. 6 and 7. The agreement with the results obtained by Besmann *et al.* comes as no surprise, since their regular interaction parameter was used.



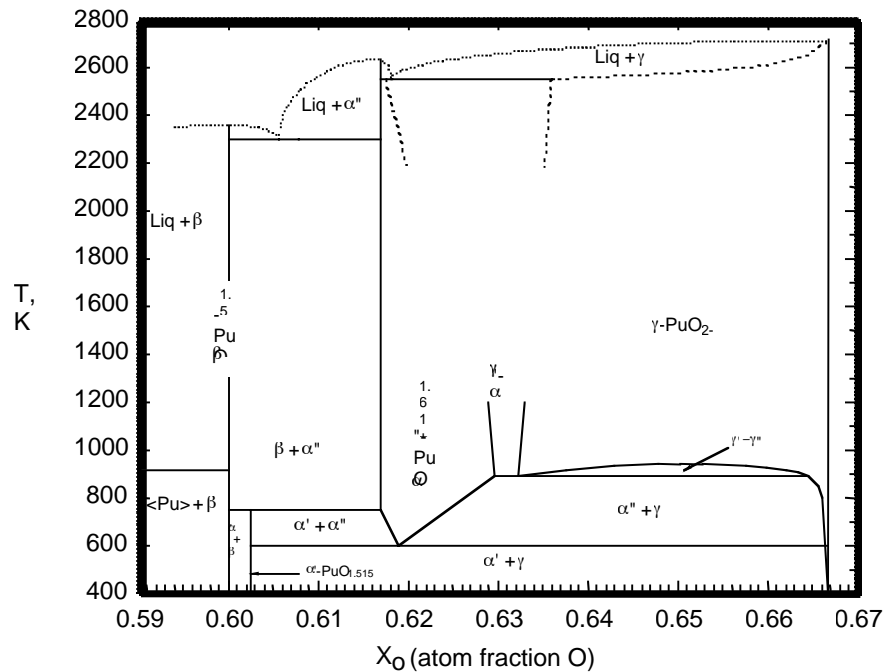
**Figure 6. Calculated partial pressure of oxygen in  $\text{PuO}_{2-}$ . For comparison, the diamonds represent the values reported in [1,2] for  $\text{PuO}_{1.8}$ .**



**Figure 7. Calculated partial pressure of oxygen in  $\text{PuO}_{2-}$ . For comparison, the diamonds represent the values reported in [1,2] for  $T = 1500$  K.**

### 3.2 Assessment of the Pu-O phase diagram

The results that have been obtained in this work can be added to the previous calculations performed by T. C. Wallace and M. Stan and reported in [24]. Unfortunately, the information is not enough to complete the assessment of the Pu-O phase diagram and more experimental and theoretical work is required. However, the Gibbs free energy of  $\text{PuO}_{2-\delta}$  is a determinant factor in calculating the phase diagram, at least in  $\text{PuO}_2$ - $\text{Pu}_2\text{O}_3$  domain. Figure 8 shows the results of the calculations in the vicinity of the  $\text{Pu}_2\text{O}_3$  compound.



**Figure 8. Calculated phase diagram of the Pu-O system.**

### 4. Conclusions

The Pu-PuN pseudo-binary phase was selected for the thermodynamic assessment of the left side of the Pu-N phase diagram. The assessment was performed using the CALPHAD method and resulted in the Gibbs free energy values of all phases. That is important for any calculations of phase equilibrium of multi-component systems that include Pu and N.

The free energy of  $\text{PuO}_{2-\delta}$  was modeled using a regular solution of  $\text{PuO}_2$  and  $\text{Pu}_2\text{O}_3$ . The model was employed for the calculation of the pressure of oxygen as a function of temperature and composition (sub-stoichiometry). The assessment of the phase diagram was possible only in the vicinity of the  $\text{Pu}_2\text{O}_3$  compound and for temperatures below 2500 K. Coupling of future experimental and thermodynamic modeling results is required to completely determine the phase diagram.

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